

Fermi Orbital Derivatives in Self-Interaction Corrected Density Functional Theory: Applications to Closed Shell Atoms

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A recent modification of the Perdew-Zunger self-interaction-correction (SIC) to the density-functional formalism¹ has provided a framework for explicitly restoring unitary invariance to the expression for the total energy. The formalism depends upon construction of Löwdin orthonormalized² Fermi-orbitals^{3,4} which parametrically depend on variational quasi-classical electronic positions. Derivatives of these quasi-classical electronic positions, required for efficient minimization of the self-interaction corrected energy, are derived and tested here on atoms. Total energies and ionization energies in closed-shell singlet atoms, where correlation is less important, using the PW92 LDA functional,⁵ are in good agreement with experiment and non-relativistic Quantum-Monte-Carlo (QMC) results albeit slightly too low.

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I. INTRODUCTION

This paper derives equations necessary for testing a new modification¹ of self-interaction corrected density functional theory⁶ and applies it to the calculation of total energies and the highest-occupied-molecular-orbital (HOMO) eigenvalues in atoms. The results show significant improvement in the HOMO-level alignments, relative to experimental ionization energies, and also show that the resulting self-interaction corrected total energies are significantly improved over density-functional approximations that do not include the self-interaction correction.

The use of localized orbital sets in quantum-mechanical calculations has a long history in both many-electron wavefunction methods and density-functional calculations. Such orbital sets are often of interest from the standpoint of chemical and physical interpretations of bonding or from the perspective of localized excitations. In density-functional-based methods^{7,8} and single-determinantal Hartree-Fock methods, many sets of physically appealing localized orthonormal orbitals may be constructed from a unitary transformation on eigenstates of the single-particle Hamiltonian or Fock matrix.⁹ Each of these orbital sets lead to the same total energy since the spin densities, spin-density matrices, and Slater determinant do not change under the action of a unitary transformation on the occupied orbital space. However, in orbital-dependent formulations such as self-interaction corrected density functional methods, the orbital dependence appearing in the expression for the total energy leads to an expression that is not invariant to unitary transformations within the occupied-orbital space. As a result, past implementations of SIC have used a double-iteration process which proceeds by first optimizing the canonical orbitals and then finding the best unitary matrix that minimizes the SIC part of the energy (Refs. 10–24). Despite a large number of implementational differences in Refs. 10–24 the general perspective of these articles is that the best possible set of localized orbitals should be found for minimizing the SIC energy. For the remainder of this paper this is referred to generically as the standard perspective or method. The auxiliary conditions required for minimization of the energy have been referred to as the localization equations^{12–14} or symmetry conditions^{19,20} and a variety of methods for solving these equations has been suggested and successfully employed. The latter references^{22–24} contains significant discussion about present and past approaches to this with a good number of applications based on modern numerical methods and also discuss the need

for consideration of complex unitary transformations (See also Ref. 21).

As an alternative to the localization-equation-based formulation, which is not explicitly invariant under unitary transformations of the occupied orbitals, Pederson, Ruzsinszky and Perdew have introduced a technique for constructing unitary matrices that explicitly depend upon the density matrix. This technique allows one to construct N localized orbitals from N quasi-classical electronic positions by first creating a set of Fermi Orbitals and then using Löwdin's method of symmetric orthonormalization to find a unitarily equivalent set of localized orbitals. The resulting orthonormal set of functions, for a small enough number of electronic shells, can coincide with Wannier functions in solids, sp^n hybrids in atoms, and Edmiston-Ruedenberg equivalent orbitals in molecules. Moreover, they have physical appearances that are similar to most of the orbitals that have been used in past SIC applications.

In Section II a brief review of the implementation of self-interaction corrections within the Perdew-Zunger formulation and the now standard approach to solving the self-consistent equations is provided. Then the equations needed for reposing the SIC functional in terms of LOs which parametrically depend on Fermi orbital centroids are presented. Within this prescription derivatives of the energy with respect to the Fermi Orbital centroids are developed. In Sec III, the method is applied to a set of closed-shell atoms with non-degenerate ground states for which the Hohenberg-Kohn theorem is strongest. The primary focus is to demonstrate that the analytical expressions are correct and to provide results on atom total energies and the highest occupied eigenvalues. In Sec IV, results are discussed and some tentative conclusions are offered.

II. ENERGIES AND DERIVATIVES WITHIN FERMI-ORBITAL SIC

Given any approximation to the density functional for the sum of the Coulomb and exchange-correlation energies denoted by $F^{approx}[\rho_\uparrow, \rho_\downarrow]$, the Perdew-Zunger self-interaction corrected expression for a spin-polarized system is written according to:

$$E^{SIC-DFT} = F^{approx}[\rho_\uparrow, \rho_\downarrow] - \sum_{i\sigma} F^{approx}[\rho_{i\sigma}, 0] \quad (1)$$

$$\rho_\sigma(\mathbf{r}) = \sum_i |\phi_{i\sigma}(\mathbf{r})|^2 = \sum_\alpha |\psi_{\alpha\sigma}(\mathbf{r})|^2 \quad (2)$$

with the N_σ localized orbital densities given by $\rho_{i\sigma}(\mathbf{r}) = |\phi_{i\sigma}(\mathbf{r})|^2$. In the above equation the localized orbitals $\{\phi_{i\sigma}\}$ are constructed from an $N_\sigma \times N_\sigma$ dimensional unitary transformation on the so-called canonical-orbital set $\{\psi_{\alpha\sigma}\}$. The canonical orbital set coincides exactly with the Kohn-Sham orbitals in the limit that the SIC vanishes. An alternative to the computationally tractable two-step procedures for variational minimization of the energy is to directly solve for the localized orbital set which must self-consistently satisfy:

$$\{H_{o\sigma} + V_{i\sigma}^{SIC}\}|\phi_{i\sigma}\rangle = \sum_j \lambda_{ij}^\sigma |\phi_{j\sigma}\rangle \quad (3)$$

$$\langle \phi_{i\sigma} | V_{i\sigma}^{SIC} - V_{j\sigma}^{SIC} | \phi_{j\sigma} \rangle = 0. \quad (4)$$

However to avoid having to solve the localization equation (Eq. 4) and restore unitary invariance, the localized orbitals may instead be derived from the Fermi orbitals (FO)^{3,4} which depend parametrically on a classical electronic position but are explicitly determined from the density-matrix:

$$F_i(\mathbf{r}) = \frac{\rho(\mathbf{a}_i, \mathbf{r})}{\sqrt{\rho(\mathbf{a}_i)}}, \quad (5)$$

$$F_i(\mathbf{r}) = \frac{\sum_\alpha \psi_\alpha^*(\mathbf{a}_i) \psi_\alpha(\mathbf{r})}{\sqrt{\{\sum_\alpha |\psi_\alpha(\mathbf{a}_i)|^2\}}} \equiv \sum_\alpha F_{i\alpha}^\psi \psi_\alpha(\mathbf{r}). \quad (6)$$

In the above equation, the classical electronic positions $\{\mathbf{a}_i\}$ then become variational parameters for minimizing the orbital-dependent part of the energy. The density of the Fermi orbital is exactly equal to the spin density at its classical centroid and it is automatically normalized since the Kohn-Sham orbitals are orthonormal. The approach suggested in Ref 1 was to use Löwdin's method of symmetric orthonormalization,² to determine an orbital set $\{\phi_{1\sigma}, \phi_{2\sigma}, \dots, \phi_{N_\sigma\sigma}\}$ than can be used to construct the SIC-DFT energy of Eq. (1).

In Ref. 1 minimization of the energy in molecules by brute force adjustment of the FO centroids lead to improved atomization energies. However, it was noted that with derivatives it would be possible to use methods such as conjugate gradients to variationally determine

the FOC. In order to do this, one starts by writing:

$$\frac{dE^{SIC}}{da_m} = \Sigma_k \{ \langle \frac{d\phi_k}{da_m} | V_k^{SIC} | \phi_k \rangle + \langle \phi_k | V_k^{SIC} | \frac{d\phi_k}{da_m} \rangle \} \quad (7)$$

$$\frac{dE^{SIC}}{da_m} = \Sigma_{kl} \{ \langle \frac{d\phi_k}{da_m} | \phi_l \rangle \langle \phi_l | V_k^{SIC} | \phi_k \rangle + \langle \phi_k | V_k^{SIC} | \phi_l \rangle \langle \phi_l | \frac{d\phi_k}{da_m} \rangle \} \quad (8)$$

$$\frac{dE^{SIC}}{da_m} = \Sigma_{kl} \epsilon_{kl}^k \{ \langle \frac{d\phi_k}{da_m} | \phi_l \rangle + \langle \phi_l | \frac{d\phi_k}{da_m} \rangle \} \quad (9)$$

$$\frac{dE^{SIC}}{da_m} = \Sigma_{kl} \epsilon_{kl}^k \{ \langle \frac{d\phi_k}{da_m} | \phi_l \rangle + \langle \phi_l | \frac{d\phi_k}{da_m} \rangle + \langle \frac{d\phi_l}{da_m} | \phi_k \rangle - \langle \frac{d\phi_l}{da_m} | \phi_k \rangle \} \quad (10)$$

$$\frac{dE^{SIC}}{da_m} = \Sigma'_{kl} \epsilon_{kl}^k \{ \langle \frac{d\phi_k}{da_m} | \phi_l \rangle - \langle \frac{d\phi_l}{da_m} | \phi_k \rangle \} \equiv \Sigma'_{kl} \epsilon_{kl}^k \Delta_{lk,m}, \quad (11)$$

with $\epsilon_{kl}^k = \langle \phi_l | V_k^{SIC} | \phi_k \rangle$. Due to the fact that the localized orbitals are constrained to lie in the space of the Kohn-Sham orbitals, this is a generally correct formula and there is no requirement that Kohn-Sham orbitals need to be self-consistent solutions of a Hamiltonian. Now to evaluate the derivatives in the above expression it is first necessary to review Löwdin's method of symmetric orthonormalization which proceeds by determining a set of orbitals, referred to here as intermediate Löwdin orbitals (ILO) by diagonalizing the overlap matrix of the Fermi orbitals according to:

$$|T_\alpha \rangle = \Sigma_j T_{\alpha j} |F_j \rangle \quad (12)$$

$$\Sigma_j S_{ij} T_{\alpha j} = Q_\alpha T_{\alpha i} \quad (13)$$

$$S_{ij} = \langle F_i | F_j \rangle \quad (14)$$

The eigenvalues of the FO-overlap matrix, Q_α , tell us how much charge each ILO captures. From Eqs. 12, 13, 14, the localized orbitals (LO), designated by ϕ_k , are constructed from the ILO and associated eigenvalues according to:

$$|\phi_k \rangle = \Sigma_{\alpha j} \frac{1}{\sqrt{Q_\alpha}} T_{\alpha k} T_{\alpha j} |F_j \rangle \equiv \Sigma_j \phi_{kj}^F |F_j \rangle \quad (15)$$

As such, it follows that:

$$|\frac{d\phi_k}{da_m} \rangle = |D_{1,km} \rangle + |D_{2,km} \rangle + |D_{3,km} \rangle \equiv \Sigma_l \Delta_{kl,m} |\phi_l \rangle, \quad (16)$$

$$|D_{1,km} \rangle = \Sigma_{\alpha j} \frac{1}{\sqrt{Q_\alpha}} T_{\alpha k} T_{\alpha j} \frac{dF_j}{da_m} = \Sigma_\alpha \frac{1}{\sqrt{Q_\alpha}} T_{\alpha k} T_{\alpha m} \frac{dF_m}{da_m}, \quad (17)$$

$$|D_{2,km} \rangle = -\frac{1}{2} \Sigma_{\alpha j} \frac{1}{Q_\alpha^{3/2}} T_{\alpha k} T_{\alpha j} \frac{dQ_\alpha}{da_m} |F_j \rangle, \quad (18)$$

$$|D_{3,km} \rangle = \Sigma_{\alpha j} \frac{1}{Q_\alpha^{1/2}} \{ \frac{dT_{\alpha k}}{da_m} T_{\alpha j} + T_{\alpha k} \frac{dT_{\alpha j}}{da_m} \} |F_j \rangle. \quad (19)$$

With quite a bit of algebra, which includes a perturbative analysis to determine quantities such as $dT_{\alpha j}/da_m$, the quantities $\langle \phi_l | D_{n,km} \rangle - \langle \phi_k | D_{n,lm} \rangle \equiv \Delta_{lk,m}^n$ are needed to evaluate Eq. 11. The full analysis will be published in a longer paper along with a discussion of scaling with system size. Here the final results are given:

$$\Delta_{lk,m}^1 = \Sigma_{\alpha\beta n} \frac{T_{\alpha k} T_{\alpha m} T_{\beta l} T_{\beta n} - T_{\alpha l} T_{\alpha m} T_{\beta k} T_{\beta n}}{\sqrt{Q_\alpha Q_\beta}} \frac{dS_{nm}}{da_m} \quad (20)$$

$$\Delta_{lk,m}^2 = \langle \phi_l | D_{2,km} \rangle - \langle \phi_k | D_{2,lm} \rangle = 0, \quad (21)$$

$$\Delta_{lk,m}^3 = -\frac{1}{2} \Sigma_{\alpha\beta n} \frac{dS_{nm}}{da_m} \{T_{\beta n} T_{\alpha m} + T_{\beta m} T_{\alpha n}\} \{T_{\alpha k} T_{\beta l} - T_{\alpha l} T_{\beta k}\} \frac{Q_\beta^{1/2} - Q_\alpha^{1/2}}{(Q_\alpha^{1/2} + Q_\beta^{1/2})(Q_\alpha Q_\beta)^{1/2}} \quad (22)$$

with $\frac{dS_{nm}}{da_m} = \langle F_n | \frac{dF_m}{da_m} \rangle \delta_{nm}$. The Kronecker delta arises because the Fermi Orbital is always normalized.^{1,3,4} Therefore only overlap integrals between different Fermi Orbitals change when the FOC of one of the Fermi Orbitals changes. The gradient of a Fermi Orbital is in fact a linear combination of the original Fermi orbitals since the Fermi-Orbital construction always leads to Fermi Orbitals that span the space of the Kohn-Sham orbitals. However it is also a linear combination of the Kohn-Sham orbitals and since these are orthonormal, the derivatives of the overlap integrals are most easily calculated by expanding the Fermi orbital derivatives in terms of the Kohn-Sham orbitals. To determine the derivatives of the Fermi-Orbital overlaps in the above expressions it is useful to use the following:

$$\nabla_{a_{i\sigma}} F_{i\sigma}(\mathbf{r}) = \frac{\Sigma_\alpha \{ \nabla_{a_{i\sigma}} \psi_{\alpha\sigma}(\mathbf{a}_{i\sigma}) \} \psi_{\alpha\sigma}(\mathbf{r})}{\sqrt{\rho(\mathbf{a}_{i\sigma})}} - \frac{F_{i\sigma}(\mathbf{r}) \nabla_{a_{i\sigma}} \rho(\mathbf{a}_{i\sigma})}{2\rho(\mathbf{a}_{i\sigma})} \equiv \Sigma_\alpha \{ \nabla_{\mathbf{a}_{i\sigma}} F_{i\alpha}^\sigma \} \psi_{\alpha\sigma}(\mathbf{r}). \quad (23)$$

$$\nabla_{a_{i\sigma}} F_{i\alpha}^\sigma = F_{i\alpha}^\sigma \left\{ \frac{\nabla_{a_{i\sigma}} \psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})}{\psi_{\alpha\sigma}(\mathbf{a}_{i\sigma})} - \frac{\nabla_{a_{i\sigma}} \rho(\mathbf{a}_{i\sigma})}{2\rho(\mathbf{a}_{i\sigma})} \right\} \quad (24)$$

The above expression shows that that the gradients of the Kohn-Sham orbitals and spin densities ultimately control the overlap integrals. As such, even a local expression for the density-functional approximation, such as the one used here, is "educated" by gradients of the density when the FO-SIC is used. With the above equations, the final expression for the derivative of the SIC energy with respect to a Fermi-Orbital centroid is given by Eq. 11 with $\Delta_{lk,m} = \Delta_{lk,m}^1 + \Delta_{lk,m}^3$.

III. APPLICATIONS TO ATOMS

For the applications discussed here the PW92 local density approximation is used and the SIC energy is constructed according to the Fermi Orbital and the functional form in the

PZ paper.⁶

$$E_{xc}^{SIC-PW92} = -\sum_{i,\sigma} \{U[\rho_{i,\sigma}] + E_{xc}^{PW92}[\rho_{i,\sigma}, 0]\}. \quad (25)$$

A modified version of NRLMOL²⁵⁻²⁷ has been used to perform the calculations. The basis used in these calculations are those determined in the original gaussian-basis-optimization method of Porezag and Pederson²⁸ which optimized basis functions for the PW92 energy functional. These basis sets differ only slightly from the current more widely distributed NRLMOL basis sets which were optimized for the PBE-GGA functional. As discussed in Ref 28, these basis sets satisfy the $Z^{10/3}$ theorem, necessary for chemically accurate converged core-level energies, and are expected to provide energies that are very close to the converged numerical energies. To obtain Fermi-Orbital derivatives that were clearly zero at the minimum, the energies were converged to 10^{-8} Hartrees. In Table II, the total energies calculated using FSIC are presented and compared to accurate Quantum Monte Carlo results^{29,30} and experiment.³¹ The total SIC energy, per spin, ranges from -0.5 to -4.0 Hartrees (in Ne and Sr respectively). In the forthcoming subsections a few more details are provided about these calculations.

Atom	PW92-LDA	FSIC(PW92)	QMC(2007)	QMC (2014)	Expt	HOMO ^{FSIC}	I_p^{expt}
Be	-14.446	-14.703	-14.646 (B)		-14.667	9.22	9.32
Ne	-128.230	-129.268	-128.892 (B)		-128.938	24.93	21.56
Mg	-199.135	-200.538	-199.986 (B)		-200.054	7.62	7.64
Ar	-525.939	-528.522	-527.391 (B)		-527.544	17.06	15.76
Ca	-675.735	-678.740	-677.377 (B)			5.99	6.11
Zn	-1776.561	-1782.059	-1779.119 (B)	-1779.342(S)		9.49	9.39
Kr	-2750.133	-2757.585	-2753.486 (B)			15.11	14.00
Sr	-3129.437	-3137.510				5.52	5.70

TABLE I. Total energies (Hartrees) of atoms for PW92-LDA, FSIC-PW92-LSDA (this work) and QMC (other work). The highest occupied eigenvalue is compared to the experimental ionization energy. All calculations in the table correspond to non-relativistic Hamiltonians. The QMC results are from Buendía *et al* and Scemama *et al* designated by B and S respectively. The experimental analysis is due to G. Martin and may be found at Ref. 31.

A. Neon and Argon

Neon and Argon represent relatively simple cases since sp^3 hybrids have already been shown to minimize the SIC energy without breaking the three-fold degeneracy of the highest-occupied orbitals. For Ne the $1s$ -centroid was placed at the origin and the $2sp$ -centroids were placed at the vertices of a tetrahedron. For Ne, the distance from the origin to the vertices of the tetrahedron was found to be 1.053 Bohrs. At this position the derivative on each Fermi-Orbital was smaller than $0.0022\text{eV}/\text{\AA}$. The $2p$ eigenvalues were found to be -24.9 eV which is in reasonable but not excellent agreement with experimental ionization potential. The total energy of -129.268 Hartree is much closer to the nonrelativistic QMC results (-128.992 to -128.938) of Buendía and experiment³¹ respectively.

For Argon, the optimized tetrahedral vertices of the $2sp$ Fermi-Orbitals were found to be at 0.391 Bohr. The $3sp$ Fermi-Orbital tetrahedral vertices were found to be at 1.345 Bohr. For Ar, at convergence the largest Fermi Orbital derivative was found to be: $0.0007\text{ eV}/\text{\AA}$ which is much smaller than necessary for convergence of the total energy. The total energy of -528.522 Hartree is again close to the QMC result and significantly improved over the LDA energies. The $3p$ eigenvalues (-17.06 eV) were found to be in good agreement with the experimental ionization energy of 15.76 eV . The results discussed in this section are in qualitative accord with the earlier exchange-only results of Pederson, Heaton and Lin.¹⁴ However the inclusion of a correlated functional leads to total energies that are even lower than experimental values.

B. Beryllium, Magnesium and Calcium

Very briefly it is useful to test the FO-method on Be since it is the simplest case for a 2-electron (per spin) system and since it is actually a challenging case for DFT. The Be atom is known to be highly susceptible to treatment of correlation due to the near degeneracy of the occupied $2s$ and unoccupied $2p$ electrons that occurs experimentally. Indeed, on a percentage basis, deviation in total energy between SIC-LSD and the QMC/experimental results is larger than for all the atoms considered here. The energies in Table 1 show that a total energy of -14.703 and a $2s$ eigenvalue of 9.22 eV which is in very good agreement with the ionization energy. For the lowest-energy configuration with vanishing Fermi-Orbital derivatives it is

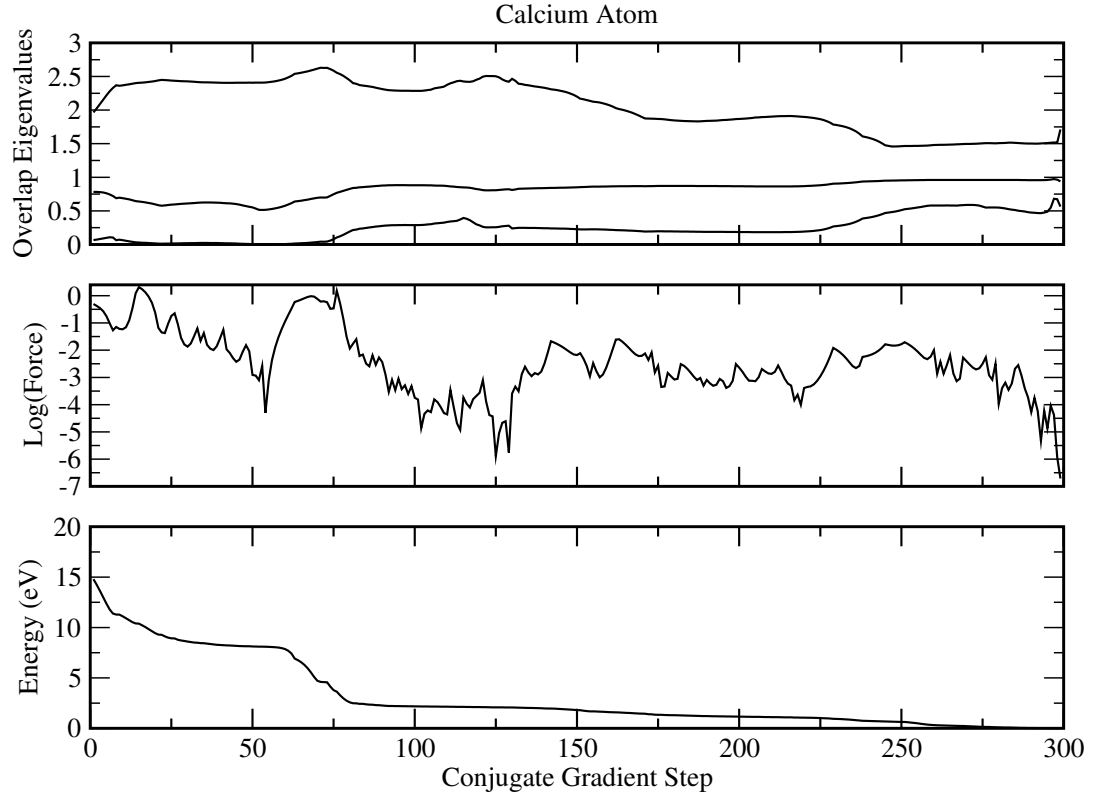


FIG. 1. Three panels show the difference of the SIC energy relative to the minimum (lower), the natural log of the norm of Fermi-Orbital gradients (middle), and information about the the lowest and highest ILO eigenvalues and geometric mean of the ILO eigenvalues is (upper). The geometric mean would be exactly unity if FOC are found that that lead to orthonormal Fermi Orbitals. Initial optimization (steps 0 to 125) constrained FOC's to have trigonal symmetry. This constraint was then completely relaxed (steps 125-300). Total SIC-LSD and LSD energies are compared to QMC results in Table 1.

verified, as expected, that the localization equations are not satisfied. This verifies that the Fermi-orbital-based formalism for SIC, with the constraint that the energy is explicitly invariant under unitary transformations, does not reduce to the standard formulation in the simplest possible limit.

This column of the periodic table presents the first case where there is a degree of geometrical frustration in determining physically appealing Fermi-Orbital centroids. In this section results for Mg and Ca are discussed but Sr is discussed in the following section as it contains $3d$ electrons. The three valences of s electrons and two valences of p electrons do not allow for simple sp^3 hybridization in this column of the periodic table.

For Mg it is found that the FOCs which minimize the energy correspond to positions that may be viewed as a tetrahedron of $3s3p^3$ hybrids with an additional FO capping one of the triangular faces. A slightly less stable solution composed of a $3s2p_z$ hybrids, a trio of $2sp_{xy}$ hybrids and an s -like Fermi-orbital was also found. The HOMO eigenvalue associated with the lowest energy solution (7.62 eV) was in much better agreement with experiment (7.64 eV) than the higher energy solution (9.52 eV). The derivatives on the FOC were again converged to a very small value (0.005 eV/Å).

For the calcium atom additional detail is provided since it has a bit more complexity than some of the lighter atoms but no $3d$ electrons. As a relatively good test of the Fermi-Orbital derivatives, the original guess for the FOCs was that the localized orbitals hybridized as a $1s$ core state, a pair of $3sp_z$ orbitals, a trio of $2sp_{xy}$ orbitals, and a quartet of $4s - 3p^3$ orbitals. Such starting points are easily accomplished by constructing sets of initial Fermi-Orbital centroids that coincide with (1) the origin, (2) a small bicapped triangular platonic solid, (3) a larger tetrahedron respectively. In Figure 1, the SIC energy (relative to the minimum) and the logarithm of the norm of the Fermi orbital gradient are shown as a function of conjugate gradient step. The figure shows that the derivatives vanish at the lowest energy.

C. Zinc, Krypton and Strontium

The author's primary motivation for returning to the self-interaction correction was that large systems containing mixtures of transition-metal ions, nearly-free-electron metal atoms, and ligands composed of first-row atoms are challenging but not insurmountable within the framework of density-functional theory.³²⁻³⁵ These challenges stem from the atom-

dependent mismatches of the chemical potential which make systematic calculations on such devices/systems difficult. Such mismatches lead to incorrect $s - d$ occupations in atoms, incorrect spin-ordering in nickel-containing molecular magnets^{34,35} and spurious charge transfer between metallic leads and molecular islands in molecular circuits.³³ Transition-metal containing systems, and their interactions with molecules composed of light atoms are also of interest to understanding catalytic processes and separation of weakly interacting gases. Such open-metal sites may be challenging since their entirely open-shell counterparts (isolated transition metal atoms) are challenging.^{36,38} In this section some preliminary results on closed shell-atoms containing d electrons are presented. The Fermi-orbital centroids are available upon request and will be broadcast, along with a simple executable version of NRLMOL-based SIC program from a website soon. Given that in one case (Mg), two low-energy solutions were found, this will allow others to look for additional solutions for these and other atoms and to help to determine whether the solutions here are indeed the absolute minima within the FO-formulation of SIC.

The total energies of these atoms are presented in Table 1 and are also found to be in good agreement with QMC results. The HOMO eigenvalues seem to be in excellent agreement with measured ionization energies. For very bad guesses of Fermi orbital positions the eigenvalues have absolutely no similarity to the converged results which reproduce, to one percent, the 3-fold and 5-fold degeneracies, expected in closed-shell atoms. It remains to be determined if, as in the case of Ne, Ar, Mg, and Ca, these degeneracies can be fully restored by the Fermi-Orbital with the best Fermi-Orbital centroids. Results from averaged SIC calculations (e.g. a slightly different functional form) suggest that such a modification could be possible.^{19,20}

IV. SUMMARY

Expressions for the derivatives of the self-interaction-corrected density-functional energy have been derived and presented. The analytic expressions are then numerically validated by showing, in conjunction with the Perdew-Zunger formulation of self-interaction corrected DFT, that the derivatives vanish when the energy is minimized and that the derivatives may be used to navigate to the minimum energy. The work here demonstrates proof of principle and, through comparison to accurate QMC results, finds that the total energies of self-

interaction corrected LDA results are improved. Based on past recollections,¹⁴ and recent discussions,³⁷ it can not yet be said that the FO-based construct will be faster than the original localization-equation-based method.^{12,14} In comparison to the real cases, the solutions are energetically very close but not identical. Consideration of the improved atomic total energies, demonstrated here, and improvements in molecular cohesive energies, demonstrated in Ref. 1, give reason for a degree of optimism. However further systematization would be desirable prior to actually optimizing a new asymptotically correct functional that is explicitly self-interaction corrected using the FO-based approach.

While the work presented here can all be reproduced (including optimizations) in a day on a laptop computer, the LDA calculations are much faster than this. It is clear that off-the-shelf conjugate-gradient methods, with initial step sizes tuned for optimization of molecular geometries, may need to be preconditioned for this type of problem and that additional work will be needed to determine when the Fermi-orbital derivatives effectively vanish (rather than the strong convergence criteria used here). Further, additional work aimed at determining transferable starting points will also need to be pursued for larger-scale applications. However, additional analysis of the functional form of the SIC energy must be performed in parallel since the numerics could become significantly easier if "softer" or nearly nodeless SIC functionals could be developed.

In regard to symmetry breakings, for closed-shell atoms devoid of d electrons, all orbital degeneracies expected from general symmetry arguments are restored by both forms of SIC. However, as for the case of the now standard SIC approach, The FO-SIC methodology does not yet lead to perfect five-fold degeneracies for closed-shell atomic systems. Even in the absence of hybridization between states of different angular momentum, it is difficult to have an orbital-by-orbital SIC correction that automatically restores the degeneracies to closed-shell d - and f - electron systems. Arguments could be made that degeneracy breaking may not be an issue since it is only the highest occupied eigenvalue that has physical meaning within DFT. On the positive side, for atoms containing d -electrons, there are clear indications that the self-interaction correction for the d electrons are much larger than for the outer s -electron. This feature is needed to account for some of the problems that have been observed in DFT-based calculations on systems where there is competition in $3d - 4s$ shell fillings.^{34,35,38} Such open-shell systems will provide good benchmark challenges for SIC methods.

The FOC-methodology, which always delivers real orbitals in closed-shell systems, leads to a conundrum since there are a variety of results, including recent applications to benzene,²³ that suggest that smoother localized densities, such as those obtained from complex orbitals, lead to better agreement with experiment. As such, the Fermi-Orbital filtering which disallows complex orbitals provides a double-edge sword. Disallowing complex Bloch functions guarantees size-extensivity in solids composed of well-separated atoms in cases where the SIC energy of an atom turns positive. Further in simple closed-shell atoms, the Fermi-orbital-based methodology will not allow for symmetry breaking of the p-orbitals for any functional since it does not allow for consideration of orbitals constructed from spherical harmonics (which lead to different SIC shifts for the $m_s = 0$ and $m_s = \pm 1$ states). However, since either the localization transformation or Fermi-orbital-based constraint must be chosen for any energy functional that exhibits any degree of orbital dependence, it is more likely that these relatively small disparities will be overcome by reconsidering the construction of the SIC energy *per se* and that the determination of whether the FO-based approach should replace the localization equations will be based upon other considerations. From the perspective of unitary invariance as a strong constraint, there seems to be a strong reason for choosing the Fermi orbital-based formulation. But on the other hand, some of the most accurate multi-configurational methods essentially proceed by accepting that unitary invariance is not the most important symmetry. This might argue for a formulation more similar to the standard perspective. In fact, the original derivation and uses of unified Hamiltonians,^{11,23} commonly used for SIC calculations since 1983, stem from even earlier use in the then nascent field of MCSCF (See Ref. 10 and 11 and references therein). Reasons for searching for new forms of the SIC functional will be discussed in an upcoming community-generated paper which carefully examines a large amount of numerical results showing promise for cases where the SIC functional is constructed from orbital densities that are in close energetic and spatial proximity to one another. The FO construction allows for the straightforward means for defining local orbital energies and determining their spatial and energetic proximity.

The average of two real localized orbital densities is of course exactly equal to the density constructed from a complex orbital determined from the same two orbitals. Perhaps a new prescription that provides a straightforward well-defined means for creating average nearly nodeless localized densities will effectively allow for the complex-localized orbitals

densities, suggested by Jónsson^{16,17,23} and Kümmel,^{18,22} and begin to address the critique provided by Kümmel that suggests that the SIC functional itself should never have densities composed of orbitals with nodes. The FO-construction provides new ways for automating the determination of localized densities so it may be that other SIC functionals which satisfy the constraints suggested in Ref. 21 are possible. Thinking about such an averaging procedure would not be inconsistent with this version of SIC or the two-step standard version of SIC since it would only change the definition of the off-diagonal Lagrange multipliers in Eq. 11. However, it is likely that the derivatives themselves would become smoother and furnish Fermi-Orbitals and SIC energies that were slightly more ambivalent to their positions.

Finally, it may also be interesting to seek numerical proof that a class of "most physical" solutions are attainable within both formulations. For example if it is possible to consider only FO's that lead to an orthonormal overlap matrix, (e.g. values of unity for all ILO eigenvalues), one would then have a set of solutions that are possible within both formulations and these solutions would almost definitely coincide with the most loved localized orthonormal orbitals in physics and chemistry. Further inquiries along these directions may very well allow for a step in the direction of merging the "road less traveled" with the "road more traveled" discussed in Ref. 21. But a significant amount of analytical work and analysis of computational results is required to address these points.

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